

## STABLE CARBON ISOTOPE ANALYSIS OF COAL/PETROLEUM COPROCESSING PRODUCTS

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### ABSTRACT

Coprocessing involves the simultaneous upgrading of coal and petroleum resid by catalytic hydroconversion. To obtain a kinetic/mechanistic description of the process, it is useful if not necessary to be able to distinguish the relative contributions of coal and petroleum to the product mixtures. In this paper, the method of stable carbon isotope ratio analysis is shown to be sufficiently sensitive to determine the relative concentrations of coal and petroleum carbon in coprocessing products. Selective isotopic fractionation does not appear to occur to a significant extent, although additional work is needed to confirm this preliminary conclusion. Application of the method to the coprocessing of Wyodak and Illinois 6 coals with a Lloydminster resid by the Signal Research/UOP process is shown to yield valid results of use in process interpretation and optimization.

### INTRODUCTION

A noteworthy recent entry in the list of developing synthetic fuels processes is the concept of coal/oil coprocessing. In coprocessing, a petroleum resid is used as the vehicle to convey coal to a reaction vessel which simultaneously converts the two to distillate mixtures which are either finished products or suitable feeds for more conventional petroleum refinery processes. The incentive for the development of coprocessing lies in its potential to replace a portion of the petroleum feedstock with a lower cost hydrocarbon source while minimizing the recycle requirements which increase the capital costs of a grassroots coal liquefaction plant. To the extent that coprocessing can be integrated with existing refinery capacity, it may find some near-term application if conventional feedstocks are unavailable. A chemical or physical synergy has also been reported by some investigators who observe better results for coprocessing than for the processing of either individual feedstock. An excellent overview of industrial and academic research in the area can be found in the preprints of the American Chemical Society's "Symposium on Coprocessing and Two-Stage Liquefaction" held at the society's Fall 1986 National Meeting (1).

In the development of hydrocarbon conversion processes, it is useful if not essential to be able to describe the hydrogenation, cracking and heteroatom (O,N,S) removal reactions which control product yields and qualities. Ideally, these reactions would be known in sufficient detail to allow a kinetic/mechanistic model to be derived which would assist in data interpretation and process optimization. For coprocessing, the development of such a model is complicated by the presence of two feedstocks greatly different in composition. The ability to distinguish the reactions of the coal and petroleum components of the feed would be a useful tool in process development.

This paper describes the validation and application of the measurement of stable carbon isotope ratios to quantitatively determine the relative concentrations of coal- and petroleum-derived components in coprocessing products. The method relies on the difference between their  $^{13}\text{C}/^{12}\text{C}$  ratios to calculate the ratio of the coal and petroleum carbon in product mixtures

containing the two. Since the carbon contents of these materials are typically 85% to 90%, this provides an excellent estimate of the overall mass compositions. The measurement of carbon isotope ratios is standard practice in the petroleum industry and its application is conceptually straightforward. However, several significant questions must be resolved. First, is the method sufficiently precise and are the differences between the carbon isotope ratios of the relevant materials large enough to obtain experimentally meaningful results? Second, does selective isotopic fractionation occur, or do all the products retain the ratio of their individual parent feedstock? Third, do actual applications confirm the utility of the method by providing meaningful process results? The work described in this paper addresses these three questions.

#### CARBON ISOTOPE RATIOS OF COAL AND PETROLEUM RESIDS

Carbon isotope ratios are determined by quantitatively converting the carbon in a sample to  $\text{CO}_2$  and measuring the relative amounts of the isotopically different  $\text{CO}_2$  species. The resulting ratio, corrected for oxygen isotopes, is compared to that of a standard material and the result is reported as the relative difference.

$$\delta = \left( \frac{(^{13}\text{C}/^{12}\text{C})_{\text{Sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{Standard}}} - 1 \right) \times 1000$$

The standard used in this work is a Peedee belemnite (PDB)(2), a Cretaceous marine organism whose shell consists of calcium carbonate. Therefore, all ratios are reported relative to PDB. Experimental details have been reported elsewhere (3).

If the carbon isotope ratios of the feedstocks are known and are not identical, the percentage of coal or petroleum carbon, for example, in a coprocessing product can be calculated as

$$\% \text{ Petroleum Carbon} = \left( \frac{\delta \text{ Sample} - \delta \text{ Coal}}{\delta \text{ Petroleum} - \delta \text{ Coal}} \right) \times 100$$

This equation requires a sufficient difference between the carbon isotope ratios of the coal and petroleum to be of practical use. Table 1 presents the  $\delta$  values for the coals and petroleum resids used in the work reported here. Despite the variation in the coal rank from subbituminous (Wyodak) to hvAb (Pittsburgh), the carbon isotope ratios of the coals are essentially the same. By contrast, the resids show a considerable range, although all have absolute values greater than those of the coals. Table 1 also provides the standard deviations, based on at least triplicate analyses, for these feedstocks. These values give a good indication of the intrinsic precision of the analytical method, and are comfortably small relative to the differences between the coal and petroleum resids.

#### VALIDATION OF METHOD

A critical assumption in the application of this method is that significant isotopic fractionation does not occur. That is, the coal- or petroleum-derived

portion of the product mixture must retain the same carbon isotope ratio as the parent feed. Although significant isotope fractionation is not expected (3), some work has been initiated to verify this assumption. In the first test, a light oil, heavy oil and vacuum resid from the LC-Fining of an Arab Heavy crude, supplied by Lummus, were analyzed. The results, shown below, indicate that the products are not substantially different. Comparison to the feed material would have been desirable, but a valid feed sample was not obtained.

<u>LC-Finer Products</u>	<u><math>\delta \pm \text{Std Dev}</math></u>
Light Oil (600°F <sup>-</sup> )	-27.01
Heavy Oil (600°F <sup>-</sup> )	-26.76
Vacuum Resid (975°F <sup>+</sup> )	<u>-26.86 <math>\pm</math> 0.11</u>
Average	-26.87 $\pm$ 0.09

In a second test of isotopic fractionation, a set of petroleum samples, supplied by R. Lett of PETC (DOE) were analyzed. These samples consisted of a Maya atmospheric tower bottoms (ATB) and its heptane soluble and insoluble fractions. The results, below, indicate the insensitivity of the carbon isotope ratio to this type of solubility fractionation.

	<u><math>\delta \pm \text{Std Dev}</math></u>
Maya ATB	-27.66 $\pm$ 0.08
Heptane Solubles	-27.66 $\pm$ 0.08
Heptane Insolubles	<u>-27.28 <math>\pm</math> 0.07</u>
Average	-27.53 $\pm$ 0.22

As a further investigation of the possibility of isotopic fractionation, products from the Wilsonville coal liquefaction pilot plant made during operations with Illinois 6 (Burning Star coal) were compared. The results below are for a first-stage vacuum tower distillate (V-178) from Integrated Two-Stage Liquefaction operations and for resids (850°F<sup>+</sup>) from two different runs. KMV-203 is a heavy deashed thermal resid from Run 245. V-131B is a pasting solvent resid from Run 247.

	<u><math>\delta \pm \text{Std Dev}</math></u>
V-178	24.14 $\pm$ 0.03
KMV-203 (Run 245, 850°F <sup>+</sup> )	23.79 $\pm$ 0.03
V-131B (Run 247, 850°F <sup>+</sup> )	<u>23.8 <math>\pm</math> 0.1</u>
Average	23.91 $\pm$ 0.20

Again, the product isotope ratios are in good agreement, despite the fact that these products were made during different runs many months apart. The isotope ratios are also in reasonable agreement with the values for Illinois 6 coal given in Table 1, although neither of these Illinois 6 samples was obtained from Wilsonville.

Finally, carbon isotope ratios were determined for two samples of Lloydminster resid provided by Signal Research/UOP. These samples were prepared by distillation of a single feedstock.

Resid	Vol % Overhead (D-1160)	mol wt (amu)	$\delta$
17-R7	5.0	1117	-29.81
18-R8	26.5	755	-29.94

Despite their considerably different boiling ranges, these resids have equivalent carbon isotope ratios.

Although these results are not definitive, they indicate that selective isotope fractionation, at least to a first approximation, is not occurring to a great extent as a result of hydroprocessing, distillation, or solubility fractionation. No gas samples were analyzed, and previous work indicates that selective isotope enrichment of the gas may be significant, particularly at low gas yields (4). However, this effect is not expected to significantly alter the carbon isotope ratios of the distillate and residual liquids which are the main reaction products. While this remains a necessary area for further investigation, the possible effects of selective isotopic fractionation are ignored, with some reason for confidence, in this report.

#### APPLICATION TO SIGNAL RESEARCH/UOP COPROCESSING RUNS

Signal Research/UOP (UOP) is developing a coprocessing technology that employs a proprietary slurry-phase catalyst in a single-stage reactor. To evaluate the utility of the carbon isotope method in a practical application, a set of four feedstock samples and vacuum overhead and toluene-soluble vacuum bottoms products from sixteen continuous coprocessing runs were obtained from UOP. The toluene-insoluble portions of the vacuum bottoms, containing unconverted coal, ash and catalyst, were removed by UOP specifically to provide samples free of their proprietary catalyst. Reaction conditions and yield data are given in Table 2. Additional data were given elsewhere (3). These data were supplied by UOP. Table 3 gives the carbon isotope analyses and coal carbon as a percentage of total carbon in the vacuum overheads and bottoms, as calculated from the carbon isotope analyses.

UOP made two sets of runs, one with Illinois 6 coal and one with Wyodak coal. All the run periods reported here used a Lloydminster resid designated 18-R8. The carbon isotope data were used to calculate the ratios of coal carbon to total carbon in the two analyzed products. By comparing these values to the percentage of coal carbon in the total feed, it is possible to calculate a "selectivity" as the ratio of the measured percentage of coal carbon to that of the feed mixture. A value greater than one indicates that the given fraction is selectively enriched in coal carbon relative to petroleum carbon; a value less than unity indicates that the fraction is relatively enriched in petroleum carbon. A value equal to one indicates that, per carbon atom, the coal and petroleum respond similarly. Figures 1 and 2 show the selectivities for the runs with Wyodak and Illinois 6 coals. The selectivities are plotted versus vacuum bottoms yields, with increasing vacuum bottoms yields generally representing decreasing processing severity. The results show a clear distinction between the two coals. For the Wyodak coal, the vacuum overheads are consistently enriched in coal carbon, while the bottoms are depleted. This indicates that, per carbon atom, the Wyodak coal is more readily converted to distillate at these conditions than the petroleum resid. The Illinois 6 coal, by contrast, shows little average selectivity for the vacuum overheads, indicating that its carbon conversion to distillate is

similar to that of the resid. There is some suggestion in the Illinois 6 data that the vacuum bottoms are depleted in coal carbon at low conversion (high vacuum bottoms yields) and enriched at high conversion. Since coal conversion from toluene insolubles to soluble resid increased with increasing severity, this increase in coal carbon may simply reflect this higher conversion.

Table 4 gives the percentages of coal carbon and petroleum carbon fed which are converted to overhead and bottoms products. These numbers are based on the carbon contents and yields of the products and their relative proportions of coal and petroleum carbon. Comparing the conversions of coal and petroleum carbon to vacuum overheads with reaction temperature (Table 2) by linear regression analysis yields the following results.

#### Coal Carbon Conversion to Vacuum Overheads

Illinois 6 Coal:      % Conv =  $-402 + 1.051 T (^{\circ}\text{C})$ ,  $R^2 = 0.89$   
Wyodak Coal:        % Conv =  $-270 + 0.778 T (^{\circ}\text{C})$ ,  $R^2 = 0.81$

#### Resid Carbon Conversion to Vacuum Overheads

Both Coals:        % Conv =  $-296 + 0.804 T (^{\circ}\text{C})$ ,  $R^2 = 0.77$

This analysis of the data underscores the significant difference in the coprocessing behaviors of the Wyodak and Illinois 6 coals. By contrast, a single linear equation appears to adequately describe the temperature response of the resid conversion regardless of the coal with which it was coprocessed. These experiments were not specifically designed to demonstrate the effect of temperature in coprocessing, and other reaction conditions were simultaneously varied. However, the results indicate that carbon isotope ratios can be used to independently assess the relative reactions of coal and petroleum in coprocessing. Additional work is required to fully exploit the value of this technique to process development.

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TABLE 1. CARBON ISOTOPE RATIOS OF COPROCESSING FEEDS

Coals	$\delta$ ‰
Illinois 6 (Burning Star)	-24.32 $\pm$ 0.07
Illinois 6 (UOP)	-24.34 $\pm$ 0.04
Wyodak (Sarpy Creek)	-24.66 $\pm$ 0.06
Wyodak (UOP)	-24.36
Pittsburgh (McElroy)	-23.80 $\pm$ 0.1
Pittsburgh (Ireland)	-23.68 $\pm$ 0.01
<u>Petroleums</u>	
Lloydminster Resid (17-R7)	-29.81
Arab Heavy Vacuum Resid	-26.21 $\pm$ 0.28
Athabasca Vacuum Resid	-29.50 $\pm$ 0.2
Maya Atmospheric Tower Bottoms	-27.66 $\pm$ 0.08

TABLE 2. OPERATING CONDITIONS, CONVERSIONS, YIELDS AND ANALYSES - UOP COPROCESSING TESTS

Test No.	Operating Conditions			Product Yields,	
	Resid/MAF Coal wt Ratio	Space Velocity (a)	T, °C	wt % of MAF Feed Vacuum Overhead	Soluble Bottoms
<u>Illinois 6 Coal</u>					
16-0915	1.5	B	414	31.6	54.7
14-0905	1.5	B	425	45.1	41.6
15-0907	1.5	B	434	49.0	38.0
4-0513	2	1.25B	425	41.0	45.5
3-0508	2	B	413	32.2	54.3
2-0502	2	B	426	48.0	39.8
6-0522	2	B	431	49.4	36.5
5-0521	2	0.75B	424	45.2	39.7
<u>Wyodak Coal</u>					
10-1111	2	1.25B	427	48.0	34.5
7-1102	2	B	414	42.0	41.0
9-1108	2	B	425	46.6	35.9
8-1107	2	B	426	48.9	35.8
12-1118	2	B	431	53.5	30.9
11-1116	2	0.75B	425	48.5	33.5

(a) Overall space velocity, based on both coal and petroleum. "B" refers to proprietary base conditions.

TABLE 3. CARBON ISOTOPE ANALYSIS - UOP COPROCESSING SAMPLES

Test No.	Carbon Isotope Analyses $\delta^{13}\text{C}$ , %		Coal Carbon as % of Total Carbon	
	Vacuum Overhead	Soluble Vacuum Bottoms	Vacuum Overhead	Soluble Vacuum Bottoms
<u>Illinois 6 Coal Products</u>				
16-0915	-27.88	-27.93	36.8	35.9
14-0905	-27.61	-27.78	41.6	38.6
15-0907	-27.60	-27.48	41.8	43.9
4-0513	-28.14	-28.13	32.1	32.3
3-0508	-28.11	-28.35	32.7	28.4
2-0502	-28.18	-27.85	31.4	37.3
6-0522	-28.21	-27.88	30.9	36.8
5-0521	-28.19	-27.87	31.2	37.0
<u>Wyodak Coal Products</u>				
10-1111	-27.89	-28.67	36.1	22.3
7-1102	-27.87	-28.86	36.4	19.0
9-1108	-27.88	-28.78	36.3	20.4
8-1107	-27.89	-28.66	36.1	22.5
12-1118	-27.83	-28.58	37.1	23.9
11-1116	-27.95	-28.46	35.0	26.1

TABLE 4. CONVERSION OF COAL AND PETROLEUM CARBON TO VACUUM OVERHEADS - SIGNAL/UOP COPROCESSING

Test No.	% Conversion to Vacuum Overhead	
	Coal Carbon	Resid Carbon
<u>Illinois 6 Coal</u>		
16-0915	30.5	33.6
14-0905	49.3	44.5
15-0907	54.2	48.5
4-0513	42.2	42.8
3-0508	33.6	33.3
2-0502	48.1	50.5
6-0522	48.6	52.3
5-0521	47.6	47.7
<u>Wyodak Coal</u>		
10-1111	60.0	46.9
7-1102	53.6	41.4
9-1108	59.5	45.5
8-1107	61.5	47.9
12-1118	68.8	51.6
11-1116	59.1	48.4

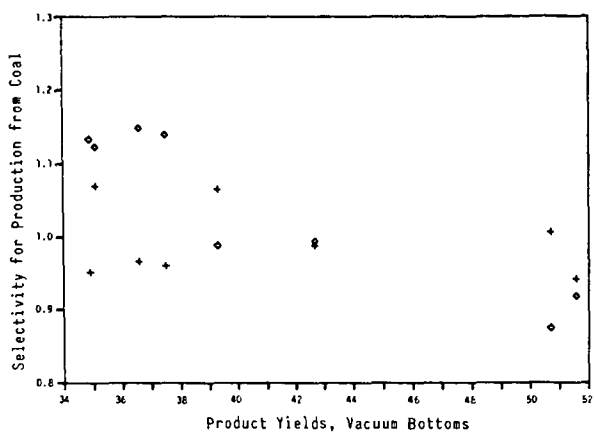


Figure 1. Selectivity vs Vacuum Bottoms Yields, UOP/Signal Research Coprocessing of Illinois 6 Coal, + - Vacuum Overhead, ◇ - Vacuum Bottoms.

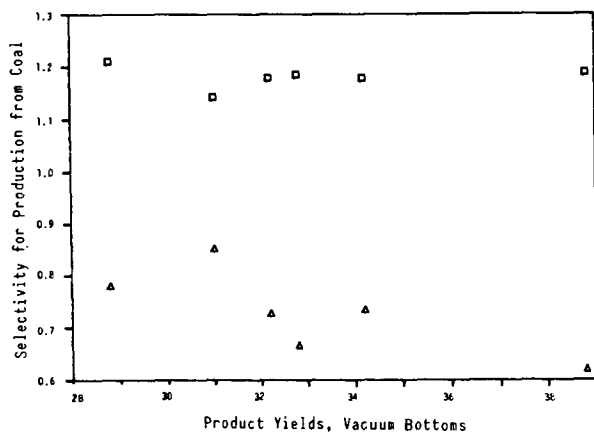


Figure 2. Selectivity vs Vacuum Bottoms Yields, UOP/Signal Research Coprocessing of Wyodak Coal, □ - Vacuum Overhead, △ - Vacuum Bottoms.